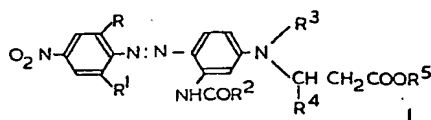


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 GB 1457532
 GB 1321902
 GB 1176798
 (58) Field of search
 C4P
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(54) Blue monoazo disperse dyes

(57) There are disclosed water insoluble monoazo dyes having the general formula:



wherein
 one of R and R' represents a nitro

group and the other represents a cyano group or both R and R' represent cyano groups, R² represents an alkyl or an aryl group, R³ represents an alkyl group, R⁴ represents an alkyl group, R⁵ represents an alkyl or cycloalkyl group which may be substituted by a halogen atom or an aryl, aryloxy, alkoxy, acyloxy or a cyano group.

There are also disclosed processes of making such dyes and their use in dyeing and printing hydrophobic fibres.

ERRATA

SPECIFICATION No. 2 104 088 A

Page 3, line 8, for dinitrobenzene read dinitro-
 azobenzene

Page 4, Example 16, Column R for Cn read CN

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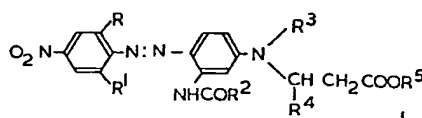
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There are also disclosed processes of making such dyes and their use in dyeing and printing hydrophobic fibres.

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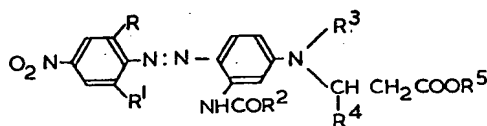
SPECIFICATION

Blue monoazo disperse dyes

The present invention relates to improvements in and relating to monoazo disperse dyes.

According to the present invention therefore, water insoluble monoazo dyes are provided having

5 the general formula:



wherein

one of R and R¹ represents a nitro group and the other represents a cyano group or both R and R¹ represent cyano groups,

10 R² represents an alkyl or an aryl group,

R³ represents an alkyl group,

R⁴ represents an alkyl group,

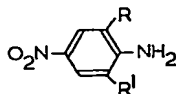
R⁵ represents an alkyl or cycloalkyl group which may be substituted by a halogen atom or an aryl, aryloxy, alkoxy, acyloxy or a cyano group.

15 The preferred dyes are those in which R⁴ represents a methyl group; and the alkyl and alkoxy groups contain one to four carbon atoms.

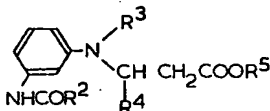
The invention also includes a process for the preparation of dyes of general formula I which comprises reacting a monoazo dye in which R and/or R¹ represents a halogen atom selected from chlorine, bromine or iodine, but preferably bromine, with cuprous cyanide. The reaction may be carried

20 out in aqueous or organic medium and advantageously in a polar aprotic solvent.

Alternatively the dyes of general formula I may be prepared by coupling one mole of the diazo compound of an amine of general formula:



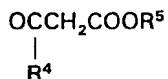
with one mole of a tertiary amine of general formula:



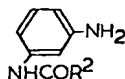
25

wherein R, R¹, R², R³, R⁴ and R⁵ have the meanings given above.

The coupling components of formula III may be prepared for example by condensation of a ketone of the formula:



30 with an amine of the formula:



and subsequent reduction of the condensation product, followed by alkylation of the resulting secondary amine.

Specific examples of amines of general formula V which may be used to prepare the coupling

35 components of general formula III are:

3-acetylaminoaniline

3-propionylaminoaniline

3-benzoylaminoaniline.

Specific examples of ketones of general formula IV are:

40 methyl acetoacetate

ethyl acetoacetate

isopropyl acetoacetate

- n butyl acetoacetate
isobutyl acetoacetate
cyclohexyl acetoacetate
benzyl acetoacetate
- 5 3-phenylpropyl acetoacetate 5
2-methoxyethyl acetoacetate
2-phenoxyethyl acetoacetate
2-acetoxyethyl-acetoacetate
2-methoxycarbonyloxyethyl acetoacetate
- 10 2-chloroethyl acetoacetate 10
2-cyanoethyl acetoacetate
methyl propioacetate
ethyl propioacetate
- 15 The invention further includes a process for the dyeing and printing of hydrophobic fibres, in which the dye is an azo dye of general formula I. 15
- As examples of hydrophobic fibres which may be dyed or printed by the further process of the invention there may be mentioned secondary cellulose acetate and cellulose triacetate, polyamide fibres such as polyhexamethylenedipamide, polyacrylonitrile fibres such as "COURTELLE" ("COURTELLE" is a Registered Trade Mark), and in particular polyester fibres such as "TERYLENE" ("TERYLENE" is a
- 20 Registered Trade Mark). Such textile materials can be in the form of thread, yarn or woven or knitted fabric. 20
- The dyes are dispersed by grinding with water and a suitable dispersing agent e.g. Dyapol SL.
- The process of the invention can be conveniently carried out by immersing the hydrophobic fibres in a dyebath comprising a dispersion of the azo dye. Dyeing is then carried out at the temperature
- 25 usually employed for the particular hydrophobic fibres. Thus in the case of secondary cellulose acetate dyeing is carried out in an aqueous bath between 60 and 85°C; in the case of cellulose triacetate fibres it is preferred to carry out the dyeing process at 95—115°C optionally in the presence of a suitable carrier e.g. an emulsion of diethyl phthalate such as that sold as "Optinol TR"; in the case of polyamide fibres dyeing is carried out at 95—100°C; in the case of polyester fibres the dyeing process can be
- 30 carried out at a temperature between 90 and 140°C; typically in the presence of a carrier, e.g. an emulsion of 2-phenylphenol such as that sold as "Optinol B" at 90 to 100°C, or in pressurised vessels at 120—140°C. 30
- Alternatively the dye dispersion may be thickened with sodium alginate or other thickeners commonly used in textile printing and applied to the synthetic textile material particularly polyester in the usual way by padding or printing with a roller or through a screen. After drying the fabric, the dye is
- 35 fixed for example by steaming at 1.0—1.7 bar pressure, or by heating the fabric in dry air at 160—220°C for 30—90 seconds or by heating at 170—180°C for 4—8 minutes with high temperature (superheated) steam. 35
- At the conclusion of the process the coloured textile material is preferably rinsed in water and/or given a treatment in an aqueous solution of soap or a synthetic detergent before being dried. It is
- 40 preferred to subject coloured polyester textile material to a treatment in an alkaline aqueous solution of sodium hydrosulphite before the soaping treatment in order to remove loosely attached dye from the surface of the material. 40
- The textile materials are coloured blue and possess good fastness to light, washing, sublimation, rubbing and dry cleaning. The dyes of the present invention are characterised by their good build up
- 45 properties on cellulose triacetate fibres. 45
- Alternatively, the dyes may be dispersed in an organic solvent, for example, chloroethylene, tetrachloroethylene or carbon tetrachloride, and colouration carried out from such a dispersion to the same fibres and under conditions of time and temperature similar to those used for aqueous application.
- 50 The colourations so obtained are equivalent in hue and fastness properties to those obtained by aqueous methods of application. 50
- The invention will be more clearly understood by reference to the following examples, in which parts and percentages are by weight.
- EXAMPLE 1
- 55 5.65 parts of 2-acetylamino-4(N-2'-ethoxycarbonyl-1'-methylethyl-N-ethyl) amino-2'-bromo-4',6'-dinitroazobenzene are dissolved in 70 parts dimethylformamide and the solution is added to a slurry of 1.14 parts cuprous cyanide in 20 parts of dimethylformamide. The mixture is stirred for four hours at room temperature and filtered. The dye is precipitated by the addition of water to the filtrate and filtered off, treated with acidified aqueous ferric chloride solution to remove copper salts, washed
- 60 with water and dried. 60
- One part of the dyestuff so obtained and two parts of Dyapol SL are added to 20 parts of water and milled in a ball mill until the average particle size of the dye is reduced to 1—5 μm , before dilution to 1000 parts with water to form a dyebath. 100 parts of polyester yarn are introduced into the dyebath at room temperature and the temperature is then raised to 130°C and maintained for one hour in a

pressurised dyeing machine. After this time the yarn is removed, rinsed and dried. The polyester fibres are dyed bright bluish red shades of very good fastness to light, washing and sublimation.

If 100 parts of cellulose triacetate are added to the dyebath prepared as above at room temperature with the addition of 3 parts of Optinol TR and dyeing is carried out for 1½ hours at

- 5 95—100°C the cellulose triacetate fibres are dyed bluish red shades characterised by very good build up properties. The fibres also possess very good fastness to light, washing and sublimation. 5

The dye 2-acetyl-amino-4-(N-(2''-ethoxycarbonyl-1''-methylethyl)-N-ethyl) amino-2'-bromo-4',6'-dinitrobenzene may be prepared by diazotising 2-bromo-4,6-dinitroaniline and coupling to N-(2''-ethoxycarbonyl-1''-methylethyl)-N-ethyl-3-acetylaminobenzene in known manner.

- 10 The N-(2''-ethoxycarbonyl-1''-methylethyl)-N-ethyl-3-acetylaminobenzene may be prepared by hydrogenating an equimolar mixture of 3-acetylaminobenzene and ethyl acetoacetate in isopropanol in the presence of a 5% palladium on charcoal catalyst and p-toluene sulphonic acid followed by ethylation with diethyl sulphate in the presence of an acid binding agent. 10



EXAMPLE 2




- 15 6.9 parts of sodium nitrite are added with stirring to 140 parts of 100% sulphuric acid, the temperature being held at 30°C by external cooling. The temperature is then raised to 70°C before cooling to 20°C when a mixture of 57.2 parts of acetic acid and 8.9 parts of propionic acid is added dropwise. 20.8 parts of 6-cyano-2,4-dinitroaniline are then added during 30 minutes at 20°C and the mixture stirred for 3 hours at this temperature. The diazo solution so obtained is added to a solution of 20 30.6 parts of N-ethyl-N-(2''-ethoxycarbonyl-1''-methylethyl)-3-propionylaminobenzene in 40 parts of 100% sulphuric acid and 500 parts of iced water at 0°C. The mixture is stirred for 1 hour when the precipitated dye 2-propionylamino-4-[N-ethyl-N-(2''-ethoxycarbonyl 1''-methylethyl)]amino-2'-cyano-4',6'-dinitroazobenzene is filtered off, washed acid free and dried. 20

- 25 One part of the dyestuff so obtained and two parts of Dyapol SL are added to 20 parts of water and milled in a ball mill until the average particle size of the dye is reduced to 1—5 µm. This is then added to a mixture of 5 parts of a galactomannan thickening agent, such as that sold as "Indalca PA3", and 5 parts of urea in 50 parts of water to form a paste which is then printed through a screen onto polyester fabric. After drying, the print is fixed by steaming for 20 minutes at 1.4 bar pressure. After this time the fabric is removed, washed and dried. The blue print so obtained has very good fastness to light, washing and sublimation. 30

The N-ethyl-N-(2''-ethoxycarbonyl-1''-methylethyl)-3-propionylaminobenzene used in example 2 may be prepared by the method described in example 1 but replacing the 3-acetylaminobenzene by 3-propionylaminobenzene.

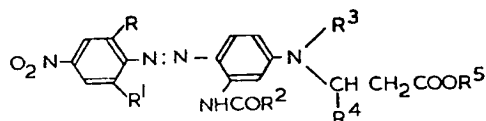
- 35 In the following table data are given referring to other monoazo dyes of the present invention corresponding to general formula II, which may be prepared by the general methods described in the previous examples, and which may be used for the dyeing and printing of hydrophobic fibres in accordance with the methods described in the previous examples. 35

Example	R	R ¹	R ²	R ³	R ⁴	R ⁵	Shade on Polyester and Cellulose Triacetate Fibres
3	NO ₂	CN	CH ₃	CH ₂ CH ₂ CH ₃	CH ₃	C ₂ H ₅	Blue
4	NO ₂	CN	CH ₃	CH ₂ CH ₂ CH ₂ CH ₃	CH ₃	C ₂ H ₅	Blue
5	NO ₂	CN	CH ₃	CH(CH ₃)CH ₂ CH ₃	CH ₃	C ₂ H ₅	Blue
6	NO ₂	CN	C ₂ H ₅	CH ₂ CH ₃	CH ₃	C ₂ H ₅	Blue
7	NO ₂	CN	CH ₃	CH ₂ CH ₃	CH ₃	CH(CH ₃) ₂	Blue
8	NO ₂	CN	CH ₃	CH ₂ CH ₃	CH ₃	CH ₂ CH ₂ CH ₂ CH ₃	Blue
9	NO ₂	CN	C ₂ H ₅	CH ₂ CH ₃	CH ₃	CH(CH ₃)CH ₂ CH ₃	Blue
10	NO ₂	CN	CH ₃	CH ₂ CH ₃	CH ₃		Blue
11	CN	CN	CH ₃	CH ₂ CH ₃	CH ₃	CH ₂ 	Blue

Example	R	R ¹	R ²	R ³	R ⁴	R ⁵	Shade on Polyester and Cellulose Triacetate Fibres
12	CN	CN	C ₂ H ₅	CH ₂ CH ₃	CH ₃	CH ₂ CH ₂ CH ₂ 	Blue
13	CN	CN		CH ₂ CH ₃	CH ₂ CH ₃	CH ₂ CH ₂ OCH	Blue
14	CN	CN	CH ₃	CH ₂ CH ₃	CH ₃	CH ₂ CH ₂ O 	Blue
15	CN	CN	CH ₃	CH ₂ CH ₃	CH ₃	CH ₂ CH ₂ OCOCH ₃	Blue
16	Cn	CN	CH ₃	CH ₂ CH ₃	CH ₃	CH ₂ CH ₂ OCOOCH ₃	Blue
17	NO ₂	CN	CH ₃	CH ₂ CH ₃	CH ₃	CH ₂ CH ₃	Blue
18	NO ₂	CN	CH ₃	CH ₂ CH ₃	CH ₃	CH ₂ CH ₂ CH ₃	Blue
19	NO ₂	CN	CH ₃	CH ₂ CH ₃	CH ₃	CH ₂ CH ₂ Cl	Blue
20	NO ₂	CN	CH ₃	CH ₂ CH ₃	CH ₃	CH ₂ CH ₂ CN	Blue

CLAIMS

1. A water insoluble monoazo dye having the general formula:



5 wherein

one of R and R¹ represents a nitro group and the other represents a cyano group or both R and R¹ represent cyano groups,

R² represents an alkyl or an aryl group,

R³ represents an alkyl group,

10 R⁴ represents an alkyl group,

R⁵ represents an alkyl or cycloalkyl group which may be substituted by a halogen atom or an aryl, aryloxy, alkoxy, acyloxy or a cyano group.

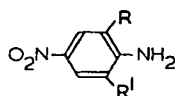
2. A dye as claimed in claim 1, in which R⁴ represents a methyl group and the alkyl and alkoxy groups contain one to four carbon atoms.

15 3. A dye as claimed in claim 1, substantially as hereinbefore described in any one of the foregoing examples.

4. A process for the preparation of a dye as claimed in claim 1 or 2, which comprises reacting a monoazo dye in which one of R and R¹ represents a halogen atom selected from chlorine, bromine or iodine, and the other of R and R¹ represents a nitro group or in which both R and R¹ represent a halogen atom selected from chlorine, bromine or iodine, and in which R², R³, R⁴ and R⁵ have the meanings given in claim 1, with cuprous cyanide.

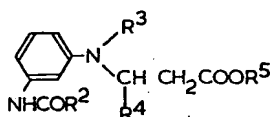
5. A process as claimed in claim 4, in which the reaction is carried out in a polar aprotic solvent.

6. A process for the preparation of a dye as claimed in claim 1 or 2, which comprises coupling one mole of the diazo compound of an amine of general formula:



wherein R and R¹ have the meanings given in claim 1, with one mole of a tertiary amine of general formula:

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III

wherein R², R³, R⁴ and R⁵ have the meanings given in claim 1.

7. A process for the preparation of a dye of the general formula I as defined in claim 1, substantially as hereinbefore described in any one of the foregoing examples.

5 8. A process for the dyeing or printing of hydrophobic fibres, in which the dye is an azo dye as claimed in claim 1, 2 or 3. 5

9. A process as claimed in claim 8 in which the hydrophobic fibres are secondary cellulose acetate, cellulose triacetate, polyamide fibres polyacrylonitrile fibres, or polyester fibres.

10 10. A process as claimed in claim 8 or 9 in which the dye is dispersed by grinding with water and a dispersing agent. 10

11. A process as claimed in claim 8, 9 or 10 which is carried out by immersing the hydrophobic fibres in a dyebath comprising a dispersion of the azo dye.

12. A process as claimed in claim 8, 9 or 10, in which the dispersion of the dye is thickened with a thickener to the hydrophobic fibre fabric by padding or printing with a roller or through a screen, the fabric is dried and the dye is fixed. 15

13. A process as claimed in claim 8 or 9, in which the dye is dispersed in an organic solvent.

14. A process for the dyeing or printing of hydrophobic fibres substantially as hereinbefore described in any one of the foregoing examples.

20 14. 15. Hydrophobic fibres whenever dyed or printed by a process as claimed in any one of claims 8 to 20

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